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# CANADIAN PATENT

⑤④ RESINS FOR USE IN CREPING PAPER

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This invention relates to new water-soluble resins and to their use in the manufacture of creped paper. This invention relates also to essentially stable aqueous solutions of these new resins of high solids content.

Creping of paper imparts extensibility characteristics thereto. Creped paper is widely used because of its high rate of relaxation. When stress is applied, tearing or breaking of the paper occurs only after a greater degree of stretch than that which occurs in uncreped paper. The creping process makes the  
10 paper more pliable and consequently more able to absorb sudden shocks without piling up stresses in the paper.

Softness is an important attribute of sanitary tissues, facial tissues, toweling and the like. These papers are often creped. Creping increases the softness by decreasing the apparent density, by decreasing the amount of fiber bonding and by increasing the elasticity and compressibility of the paper.

Several methods are employed in the art to crepe paper. One means of imparting extensibility characteristics (crepe) to paper sheeting is often referred to in the art as "blade creping".  
20 Blade creping is usually accomplished during the drying process of the papermaking procedure. Thus, for example, as the paper leaves the press section of a fourdrinier machine, it contains about 30% to 35% solids. The drying process consists of supplying sufficient heat to the paper to evaporate most of the water remaining in the sheet after wet pressing. Drying is usually accomplished by passing the sheet over the surface of a heated drum. After the desired amount of water has been removed from the paper sheet, the paper is separated and removed from the surface of the heated drum by means of a doctor blade. The paper is creped dur-  
30 ing its separation and removal from the heated drum by means of the doctor blade. The creped paper can be further dried if required. Subsequently the dried creped paper is wound onto a mandrel in the form of a roll for subsequent handling, storage, or the like.



Another means of creping paper is sometimes referred to in the art as "roll creping". The roll creping process is essentially the same as the blade creping process with the exception that the takeoff or removal of the paper from the heated drum is accomplished by means of a rubber covered mandrel. During removal of the paper sheet it is passed between the nip formed by the rubber covered mandrel and the heated drum. The heated drum travels about two times faster than the rubber mandrel. Because of the high differential speed, pressure at the nip is essentially 0.

10 Creping of the paper sheet results when it is removed from the heated drum in this manner.

The key to the creping of paper by either of the above two methods is the adhesion of the paper to the heated drum. This adhesion must be carefully controlled. If adhesion is inadequate, the paper sheet will be too easily removed from the surface of the drum, resulting in little or no creping of the paper. If the adhesion is such that the sheet adheres too tenaciously to the heated drum, a substantial amount of internal fiber bonding will be disrupted or destroyed during creping, whereby the

20 strength properties of the creped sheet are reduced substantially. A resinous adhesive is sometimes applied to the surface of the heated drum to promote the desired adhesion of the paper to the drum surface. In some procedures the adhesive is applied, either externally or internally, to the paper sheet prior to contacting the surface of the heated drum. It is difficult to obtain and maintain the desired adhesion with some resinous adhesives. Some desirable resinous adhesives impart wet-strength properties to the creped paper which is undesirable in certain creped papers, such, for example, as toilet tissue.

30 In accordance with this invention there are provided novel water-soluble resins adapted particularly for use in the creping of paper. The resins provide highly satisfactory and controllable adhesion to the heated drum in the creping operation. In addition, the resins of this invention impart little, if any,

wet strength to the creped paper. The substantial absence of wet strength is of particular importance in the manufacture of toilet tissue.

The novel resinous compositions of this invention are cationic and are water-soluble. Aqueous solutions of the resins are employed in the manufacture of creped paper by the procedures described above.

According to this invention, a water-soluble resin derived by (1) alkylating from about 75% to 100% of the secondary amine nitrogens of a polyaminopolyamide containing secondary amine nitrogens to provide an alkylated polyaminopolyamide, (2) adding to an aqueous medium of the alkylated polyaminopolyamide from about 0.10 to about 0.33 mole of epichlorohydrin per mole of amine nitrogen of the alkylated polyaminopolyamide, and (3) heating the reaction mass to a temperature of from about 30°C. to about 90°C. until substantially all epichlorohydrin has reacted, the said polyaminopolyamide being derived by reaction of a dicarboxylic acid and a polyalkylene polyamine of the formula



where n is an integer 2 through 6 and x is an integer 1 through 4. The polyaminopolyamides and their method of manufacture are detailed more fully hereinafter.

The polyaminopolyamide is reacted with an alkylating agent in an aqueous medium having an initial pH of from about 6 to about 12 at a temperature of from about 40°C. to about 200°C. Preferred pH is about 8 to about 11. The amount of alkylating agent employed will be that sufficient to alkylate from about 75% to 100% of the secondary amine nitrogens of the polyaminopolyamide. This will usually require at least .75 mole of alkylating agent per mole of secondary amine nitrogen of the polyaminopolyamide. Any amount of alkylating agent in excess of that required to alkylate 100% of the secondary amine nitrogens will form quaternary ammonium nitrogens with the alkylated nitrogens. In preparing the resins of this invention the amount of quaternary ammonium nitrogens resulting from an excess of alkylating agent should not exceed about 20% of the secondary amine nitrogens originally present in the polyaminopolyamide.

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Compounds that can be employed as alkylating agents in carrying out this invention include dimethyl sulfate; diethyl sulfate; dipropyl sulfate; methyl chloride; methyl iodide; methyl bromide; ethyl bromide; propyl bromide; the mono-, di- and tri-methyl phosphates; the mono-, di- and tri-ethyl phosphates; and the mono-, di- and tri-propyl phosphates.

In another aspect of this invention, the secondary amine nitrogens can be methylated by reaction of the polyaminopolyamide with formaldehyde and formic acid. The reaction is carried out in aqueous medium and during reaction the system is maintained at a pH of from about 1 to about 6. The formaldehyde and the formic acid are added to the aqueous medium containing the polyaminopolyamide in amounts sufficient to methylate at least about 75% of the secondary amine nitrogens of the polyaminopolyamide. Temperature of the aqueous reaction medium is maintained at about 10 40°C. to about 100°C. during reaction. While it is possible to methylate 100% of the secondary amine nitrogens of the polyaminopolyamide in this reaction, any amount of formaldehyde and formic acid in excess of that required for 100% methylation will not result in the formation of quaternary nitrogens. Thus, in this aspect of the invention, no quaternary nitrogens are formed. While any organic acid or inorganic acid can be used to maintain the desired pH of the reaction medium, it is preferred, for the purposes of this invention, to use formic acid for this purpose. Thus, in carrying out this invention, the amount of formic acid 20 employed will be in excess of that amount stoichiometrically equivalent to the amount of formaldehyde employed, the excess being that required to maintain the desired pH of the reaction medium.

The alkylated polyaminopolyamide is subsequently reacted with epichlorohydrin in aqueous medium at a pH of from about 7 to about 11 at a temperature of from about 30°C. to about 90°C. for a period of time of from about 5 minutes to about 6 hours. Time varies inversely with temperature. Preferred temperature is in the range of from about 40°C. to 70°C. 30 The time of reaction at these temperatures will be from about 1/2 to 2 hours. In any event reaction is carried out until substantially all epichlorohydrin reactant has reacted.

In preparing the aqueous reaction medium, it is desirable that essentially all the polyaminopolyamide be dissolved

therein. A water miscible alcohol such, for example, as methanol, ethanol, propanol, isopropanol, and t-butanol, can be added to the aqueous medium to complete dissolution of those polyaminopolyamides that are not completely water soluble. The amount of alcohol employed will be that required to provide for substantially complete dissolution of the polyaminopolyamide.

In the alkylated polyaminopolyamide--epichlorohydrin reaction, the amount of epichlorohydrin employed is important and will be from about .10 mole to .33 mole of epichlorohydrin per 10 mole amine nitrogen of the alkylated polyaminopolyamide and preferably from about 0.20 mole to 0.30 mole.

The polyaminopolyamide employed in carrying out this invention is derived by reaction of a polyalkylene polyamine and a dicarboxylic acid. The dicarboxylic acid is reacted with the polyalkylene polyamine under conditions such as to produce a long chain polyaminopolyamide.

Suitable dicarboxylic acids that can be used to prepare the polyaminopolyamide include diglycolic acid and the saturated aliphatic dicarboxylic acids containing from 4 through 10 carbon atoms, such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid.

Other suitable dicarboxylic acids include terephthalic acid, isophthalic acid, and alpha-unsaturated dicarboxylic acids such as maleic acid, fumaric acid, itaconic acid, glutaconic acid, citraconic acid, and mesaconic acid.

The available anhydrides of the above acids can be used in preparing the polyaminopolyamide as well as the amides thereof. Esters of the above acids can be employed in preparing the polyaminopolyamide. Another ester that can be used is an ester of malonic acid such, for example, as dimethyl malonate, diethyl malonate, and dipropyl malonate. Mixtures of any two or more of the above reactants can be used to prepare the polyaminopolyamides, if desired. Thus, for example, a mixture of two different acids can be used; a mixture of two different anhydrides can

be used; a mixture of two different esters can be used; a mixture of two different amides can be used; a mixture of at least one acid and at least one ester can be used; a mixture of at least one anhydride and at least one acid can be used; and a mixture of at least one acid, at least one anhydride, and at least one ester can be used.

The polyalkylene polyamine employed will have the formula



10 wherein n is an integer 2 through 6 and x is an integer 1 through

4. Specific examples of polyalkylene polyamines that can be employed include diethylenetriamine, triethylenetetramine, tetraethylene pentamine, dipropylenetriamine, dihexamethylenetriamine, pentaethylenehexamine, and iminobis(propylamine). Mixtures of two or more alkylene polyamines can be used if desired.

The spacing of the secondary amine nitrogens in the polyaminopolyamide can be increased if desired. This can be accomplished by substituting a diamine such as ethylenediamine, 1,3-diaminopropane, 1,2-diaminopropane, hexamethylenediamine and the  
20 like for a portion of the polyalkylene polyamine. For this purpose, up to about 60% of the polyalkylene polyamine can be replaced by a molecularly equivalent amount of diamine.

Temperatures employed in carrying out reaction between the dicarboxylic acid and the polyalkylene polyamine can vary from about 110°C. to about 250°C. or higher at atmospheric pressure. Temperatures between about 160°C. and 210°C. are preferred. If reduced pressure is employed, lower temperatures can be used. The time of reaction will be from about 1/2 hour to 2 hours and will vary inversely with temperature.

30 In carrying out the reaction, it is preferred to use an amount of dicarboxylic acid sufficient to react with substantially all the primary amine nitrogens of the polyalkylene polyamine but insufficient to react with the secondary amine nitrogens to any substantial extent. This will usually require a mole

ratio of polyalkylene polyamine to dicarboxylic acid of from about 0.9 to 1 to about 1.2 to 1. Preferred mole ratios are from about 0.92:1 to 1.14:1.

The following examples are illustrative of this invention. In the examples parts and percentages are by weight.

Example 1

Diethylenetriamine, 100 parts, and water, 50 parts, are placed in a reaction vessel equipped with a motor-driven stirrer, thermometer and condenser. To this is added 146 parts adipic acid. After the acid has dissolved in the diethylenetriamine, the resulting solution is heated and maintained at a temperature of from about 170°C. to 175°C. for 1-1/2 hours. The reaction mass is cooled to room temperature and is diluted with water to a solids content of about 75%. To 50 parts of a 50% solids solution of the above polyaminopolyamide which has a reduced specific viscosity = 0.155 ( $\eta_{sp}/C$  at  $C = 2$  g./100 ml., in 1 M  $\text{NH}_4\text{Cl}$  at 25°C.) are added 13.8 parts 88% formic acid and 10.5 parts 37% formaldehyde. The resulting mixture is heated slowly to reflux, boiled under reflux for 1 hour, then cooled, diluted with 45 parts water, and adjusted to about pH 8.5 with 10 N  $\text{NaOH}$ . To this reaction mass is added 2.7 parts epichlorohydrin. The resulting mass is heated at 60-65°C. for 1.1 hours, while the viscosity of the mixture increases to Gardner-Holdt reading "M" (of a sample cooled to 25°C.). The solution after dilution with 246 g. water and adjustment to pH 4 with  $\text{H}_2\text{SO}_4$ , has a Brookfield viscosity of 29 centipoises at 25°C. (Brookfield Model LVF Viscometer No. 1 spindle, 60 rpm.).

The above resin solution is employed to crepe paper by the blade creping process with highly satisfactory results. The resin solution is added at the wet end of the papermaking process and prior to sheet formation. The amount of resin solution employed will be that sufficient to supply from about 0.01% to about 1%, and preferably from about 0.1% to about 0.2%, by weight, based on the dry weight of the paper pulp. Addition of the resin

solution can be made to the fan pump, refiner, machine chest and the like.

#### Example 2

To a resin kettle equipped with anchor stirrer, nitrogen sparge tube, thermometer, and distilling head are charged 61.9 parts (0.60 mole) diethylenetriamine, 16.2 parts (0.27 mole) ethylenediamine, 19.77 parts (0.267 mole) 1,3-diaminopropane, and 175.2 parts (1.20 moles) adipic acid. The mixture is heated to 175°C., and maintained there for 4 hours while 39.7 parts distillate is collected. A viscous reaction mass is produced which is diluted with about 220 parts of 80°C. water and cooled to give a 52.2% solids solution. The polyaminopolyamide has a reduced specific viscosity (RSV) = 0.142 ( $=\eta_{sp}/C$  in aqueous 1 M  $\text{NH}_4\text{Cl}$  at 25°C., where  $C = 2$  g. solids/100 ml. solution). To 47.9 parts of the above solution are added 2.1 parts water, 7.7 parts 88% formic acid and 5.85 parts 37% formaldehyde. The resulting mixture is heated to 100°C. and boiled under reflux for 1 hour, cooled, and adjusted to pH 8.5 with 6.7 parts 50% NaOH. To the resulting solution is added 1.48 parts epichlorohydrin to provide a solution which is subsequently heated at 74-78°C. for 3.6 hours and then cooled to room temperature. The resulting resin solution contains 38.1% solids and can be employed in the creping of paper by the blade creping process with good results.

#### Example 3

A stirred mixture of 151.4 parts (0.80 mole) tetraethylene pentamine, 35.0 parts water, and 134.8 parts (0.667 mole) sebacic acid is heated at 170-183°C. for about 1.7 hours with the evolution of 57.06 parts of aqueous distillate. The resulting polyaminopolyamide is decanted and cooled to room temperature. The polymer has an RSV = 0.24 (measured as a 2 g./100 ml. solution in 1 M  $\text{NH}_4\text{Cl}$  at 25°C.). To 25 parts of the polyaminopolyamide thus prepared are added 27.5 parts isopropyl alcohol, 35 parts water, and 24.9 parts 88% formic acid. The resulting solution is treated with 18.9 parts 37% formaldehyde and boiled for 1 hour

under reflux conditions. The mixture is then adjusted to pH 8.5 with 24.2 parts 50% NaOH, diluted with 35 parts water and 27.5 parts isopropyl alcohol, and 4.8 parts epichlorohydrin is added thereto. The mixture is heated at 65°C. for 2.5 hours, then diluted with 250 parts H<sub>2</sub>O to give a 12.85% solids resin solution which can be employed in the creping of paper by the blade creping process with good results.

#### Example 4

To a stirred solution of 50 parts of an aminopolyamide, 10 RSV = 0.16, (derived from a 1:1 mole ratio of diethylenetriamine and adipic acid, heated for approximately 1.5 hours at 170-175°C. with distillation of water) in 150 parts water, is added 29.5 parts dimethyl sulfate over a 10 minute period. The resulting mixture is warmed for 1 hour at 50°C. and then adjusted to pH 10 with 50% NaOH. The resulting mixture is cooled to 40°C., and 5.32 parts epichlorohydrin is added. The resulting mixture is heated to about 63°C. for 28 minutes during which time the Gardner-Holdt viscosity (of a sample cooled to 25°C.) rises to M. The mixture is then diluted with 622 parts water and adjusted to pH 4.0 with 20 H<sub>2</sub>SO<sub>4</sub> to give a resin solution of 11.7% solids content, which solution can be employed in the creping of paper by the blade creping method with good results.

#### Example 5

A mixture of 200 parts diethylenetriamine, 200 parts water and 260.2 parts itaconic acid is heated to 168-175°C. for 1.8 hours, by which time 257 parts aqueous distillate is collected. To a solution of 25 parts of the above polyaminopolyamide in 25 parts water are added 13.85 parts 88% formic acid and 10.5 parts 37% formaldehyde. The mixture is boiled under reflux conditions for 1 hour, cooled, adjusted to pH 8.5 with 11.6 parts 50% NaOH and diluted with 90 parts water. To this solution is added 2.76 parts epichlorohydrin. The resulting mixture is heated at 65-75°C. for 5.25 hours. The pH of the reaction mass is then re-adjusted to 11 with 1.4 parts 50% NaOH, and heating is continued

at 65-75°C. for an additional 1.6 hours. The resulting solution contains 25.4% total solids and can be used in the creping of paper by the blade creping process with good results.

The resins of the above examples impart little, if any, wet strength to the creped paper in which they are employed.

The above description and examples are illustrative of this invention and not in limitation thereof.

1. A water-soluble resin derived by (1) alkylating from about 75% to 100% of the secondary amine nitrogens of a polyaminopolyamide containing secondary amine nitrogens to provide an alkylated polyaminopolyamide, (2) adding to an aqueous medium of the alkylated polyaminopolyamide from about 0.10 to about 0.33 mole of epichlorohydrin per mole of amine nitrogen of the alkylated polyaminopolyamide, and (3) heating the reaction mass to a temperature of from about 30°C. to about 90°C. until substantially all epichlorohydrin has reacted, the said polyaminopolyamide being derived by reaction of a dicarboxylic acid and a polyalkylene polyamine of the formula



where n is an integer 2 through 6 and x is an integer 1 through 4.

2. The water-soluble resin of claim 1 wherein the secondary amine nitrogens of the polyaminopolyamide are methylated by reaction with formaldehyde and formic acid.

3. The water-soluble resin of claim 1 wherein the amount of epichlorohydrin is from about 0.20 mole to about 0.30 mole.

4. The water-soluble resin of claim 2 wherein the amount of epichlorohydrin is from about 0.20 mole to about 0.30 mole.

5. The water-soluble resin of claim 1 wherein the polyaminopolyamide is derived from adipic acid and diethylenetriamine.

6. The water-soluble resin of claim 1 wherein the polyaminopolyamide is derived from adipic acid and triethylenetetramine.

7. An aqueous solution of the water-soluble resin of claim 1.

8. An aqueous solution of the water-soluble resin of claim 2.
9. An aqueous solution of the water-soluble resin of claim 3.
10. An aqueous solution of the water-soluble resin of claim 4.
11. In the method of creping paper wherein an adhesive is employed to provide for adherence of paper sheeting to a drum drier prior to separation therefrom by separation means, said separation means providing for creping of the paper, the improvement wherein the resin of claim 1 is employed as the adhesive.
12. In the method of creping paper wherein an adhesive is employed to provide for adherence of paper sheeting to a drum drier prior to separation therefrom by separation means, said separation means providing for creping of the paper, the improvement wherein the resin of claim 2 is employed as the adhesive.
13. In the method of creping paper wherein an adhesive is employed to provide for adherence of paper sheeting to a drum drier prior to separation therefrom by separation means, said separation means providing for creping of the paper, the improvement wherein the resin employed as the adhesive is a water-soluble resin derived by (1) alkylating from about 75% to 100% of the secondary amine nitrogens of a polyaminopolyamide containing secondary amine nitrogens with an alkylating agent selected from the group consisting of dimethyl sulfate; diethyl sulfate; dipropyl sulfate; methyl chloride; methyl iodide; methyl bromide; ethyl bromide; propyl bromide; the mono-, di- and tri-methyl phosphates; the mono-, di- and tri-ethyl phosphates; and the mono-, di- and tri-propyl phosphates or by reaction with formaldehyde and formic acid, to provide an alkylated polyaminopolyamide, (2) adding to an aqueous medium of the alkylated polyamino-polyamide from about 0.10 to about 0.33 mole of epichlorohydrin per mole of amine nitrogen of the alkylated polyaminopolyamide, and (3) heating the reaction mass to a temperature of from about 30°C. to about 90°C. until substantially all epichlorohydrin has

reacted, the said polyaminopolyamide being derived by reaction of a dicarboxylic acid and a polyalkylene polyamine of the formula  $H_2N(CH_2)_n(NHC(=O)CH_2)_xNH_2$  where n is an integer 2 through 6 and x is an integer 1 through 4.

14. The method of claim 13 wherein the secondary amine nitrogens of the polyaminopolyamide are methylated by reaction with formaldehyde and formic acid.

15. The method of claim 13 wherein the amount of epichlorohydrin is from about 0.20 mole to about 0.30 mole.

16. The method of claim 14 wherein the amount of epichlorohydrin is from about 0.20 mole to about 0.30 mole.

17. The method of claim 13 wherein the polyaminopolyamide is derived from adipic acid and diethylenetriamine.

18. The method of claim 13 wherein the polyaminopolyamide is derived from adipic acid and triethylenetetramine.

